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Disproportionation-Inspired Construction of Highly Functionalized Bicyclo[3.2.1]octanes

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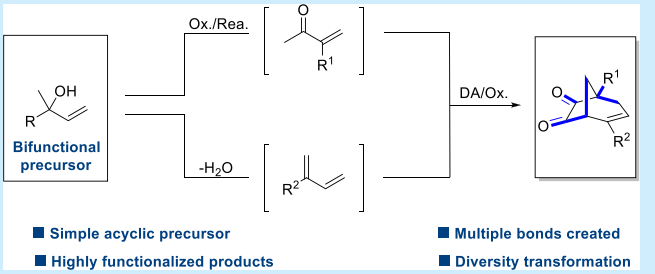
ABSTRACT: The formation of one unavoidable byproduct in traditional disproportionation reactions limits their applications in synthesis. Inspired by convergent disproportionation, we develop an iodine-induced cyclization and oxidation of allylic alcohols to produce highly functionalized bicyclo[3.2.1]octanes through creation of six new bonds. Guided by the mechanism, we elaborated a variety of other bicyclo[3.2.1]octanes bearing distinct groups with presynthesized dienes and enones as the starting materials. This work provides a divergent access to bicyclo[3.2.1]-octane frameworks.



Except for intermolecular reactions, most organic reactions involve more than one component to give target products (Figure 1a). As a unique reaction, the disproportionation reaction could offer the oxidation product and reduction product simultaneously from only one reactant.[1] However, the formation of one unavoidable byproduct (A^1_{ox} or A^1_{red}) in disproportionation reactions limits their applications (Figure 1a). If products A^1 and A^2 could react further to offer complex product C in one pot, it will undoubtedly greatly improve the efficiency and atom economy of the reaction (Figure 1a). This proposed convergent disproportionation strategy is challenging but has great potential for wider applications.

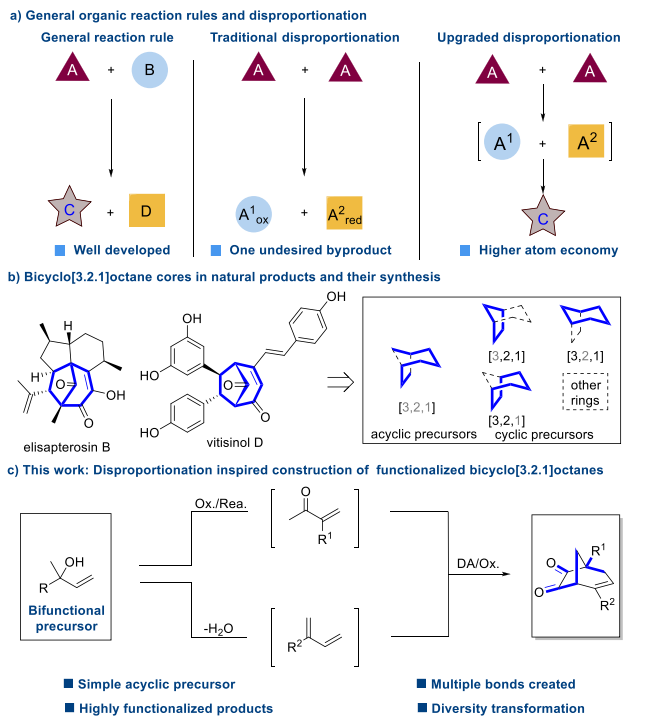


Figure 1. Disproportionation-inspired construction of bicyclo[3.2.1]-octanes from allylic alcohols.

Meanwhile, a highly functionalized bicyclo[3.2.1]octane skeleton is the basic framework of numerous important biologically active natural products (Figure 1b), including sesquiterpenes,[2] diterpenes,[3] lignans,[4] alkaloids,[5] and antibiotics.[6] In addition, functionalized bicyclo[3.2.1]octane derivatives have proven to be powerful building blocks in total synthesis.[7] Hence, the past decade has witnessed tremendous progress in the construction of such important frameworks. Generally, bicyclo[3.2.1]octane moieties are accessed from acyclic and cyclic precursors (Figure 1b).[8] Although intramolecular annulation of acyclic precursors to obtain bicyclo[3.2.1]octane framework is attractive, the precursors are complicated in terms of preparation.[9] Therefore, developing a complementary approach to construct a functionalized bicyclo[3.2.1]octane moiety through intermolecular reaction from a simple acyclic precursor would be of great interest.

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To address the aforementioned issues, we herein develop a reaction to concisely construct highly functionalized bicyclo[3.2.1]octanes through formation of six new bonds with the advantage of a convergent disproportionation (Figure 1c). This protocol uses easily available allylic alcohols as bifunctional precursors. Moreover, the obtained highly functionalized bicyclo[3.2.1]octane products have been demonstrated as key intermediates in many interesting transformations.

We began our investigation by treating 2-phenylbut-3-en-2-ol (**1a**) in the presence of iodine and DMSO, which is a mild oxidation system.[10] To our delight, a small amount of bicyclo[3.2.1]octane **2a** was detected (Table S1). While increasing the amount of iodine proved to be beneficial (Table S1, entries 1−5), the use of 1.2 equiv of iodine with respect to **1a** gave the best result, and **2a** was obtained in 42% yield (entry 4). The temperature examination suggested that 100 °C was optimal for this process (entries 4 and 6−8). Other solvents, such as toluene, ethyl acetate, 1,4-dioxane, and DMF, all failed to produce the desired product (entries 9−12, respectively). The use of molecular sieves suppressed this reaction (entry 13). The addition of water had no obvious effect on the reaction (entry 14). In the presence of I_2 and DMSO, the formation of thiophene and a homo-Diels−Alder cycloaddition product from a diene intermediate was observed.[11] Considering that the diene produced from **1a** may polymerize, a radical inhibitor was added, but no desired product was obtained in the presence of BHT (entry 15). To our delight, the reactivity for **2a** was further enhanced when the reaction was performed under a nitrogen atmosphere at a higher concentration (entry 16).

With the optimized conditions in hand, the scope of this transformation was investigated (Figure 2). The reaction could be carried out with a series of substituted aryl allylic alcohols, affording the corresponding products in acceptable yields. For instance, 2-phenylallyl alcohols with weak electron-donating substituents, such as Me, Et, ^{t}Bu, and Cy, at the *para* or *meta* position of the phenyl ring all reacted smoothly under the current condition and gave **2b−2f** in moderate yields (46−52%). Notably, substrates bearing halide groups, including F, Cl, and Br, were well tolerated, delivering **2g−2i**, respectively, in 35−43% yields. A substituent at the *meta* position of the phenyl ring was amenable to transformation, as well (**2j**). Moreover, the naphthyl-substituted allylic alcohol was suitable for this process, leading to **2k** in 45% yield. A substrate with a strong electron-donating functional group (methoxy) provided the corresponding product in a lower yield (**2l**). However, an alkyl-substituted allylic alcohol could not afford the target product (**2m**). It is notable that six new bonds were created during the formation of these highly functionalized bicyclo[3.2.1]octanes.

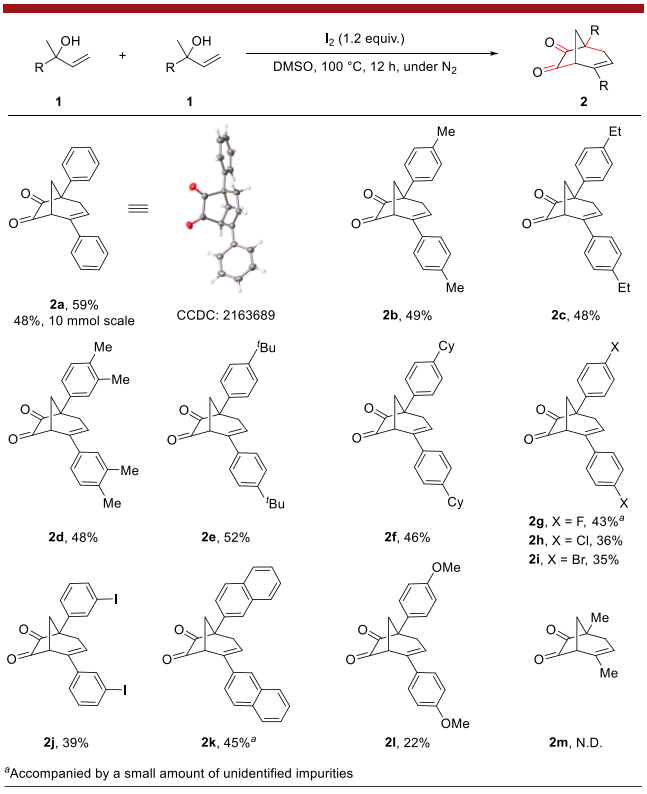

Figure 2. Substrate scope.

To illuminate the mechanistic details and improve the generality of this protocol, several control experiments were thereby performed (Figure 3). When the reaction was carried out at room temperature, possible intermediates **3a** and **4a** were detected (Figure 3a, eq 1). However, neither **3a** nor **4a** could be converted to target product **2a** under standard conditions (Figure 3a, eqs 2 and 3). By contrast, a combination of diene **3g** and enone **4a** successfully led to cross-coupling product **5a** (Figure 3a, eq 4). This suggests that both diene **3** and enone **4** are key intermediates for the formation of bicyclo[3.2.1]octane. According to our previous work,[11] an allylic alcohol could undergo dehydration easily to produce a diene. To determine the generation pathway of enone, a related experiment was conducted (Figure 3b). The observation of enone **6o** and **6o′** from substrate **1o** suggests that the enone is rearranged from the allylic alcohol. Conventionally, alkyl groups are difficult to migrate,[12] which explains why **2m** cannot be obtained. On the basis of the results presented above, we surmise that the product of the Diels−Alder reaction between diene and enone is another key intermediate. To test this hypothesis, Diels−Alder cycloaddition product **7a** was synthesized for the control experiment. It was found that **5a** could be obtained in 67% yield from **7a** in the presence of iodine and DMSO (Figure 3c, eq 6). In addition, iodinated product **8a** was well converted into target product **5a** (Figure 3c, eq 7). These results suggest that **7a** and **8a** might be the crucial intermediates for the formation of **5a**. The free radical termination experiment shows that intramolecular ring closure reaction of **7a** is probably a free radical process (Figure 3d, eq 8).

On the basis of the aforementioned observations and previous reports,[11] a plausible mechanism for the construction of highly functionalized bicyclo[3.2.1]octane is shown in Figure 3e. Initially, allylic alcohol **1** proceeds through dehydration to produce diene intermediate **3**. Meanwhile, allylic alcohol **1** can also undergo semipinacol rearrangement through intermediate **A** with the aid of iodine to form ketone **9**. Next, the elimination of hydrogen iodide from **9** yields enone **4**, which reacts with diene **3** to produce Diels−Alder cycloaddition product **7**. The hydrogen iodide could be oxidized by DMSO to regenerate iodine.[13] In the presence of iodine and DMSO, α-iodo ketone **8** is easily transformed into intermediate **10** through Kornblum oxidation. With iodine as the radical initiator, 2-oxoaldehyde **10** is transformed into radical intermediate **B**, which undergoes a subsequent

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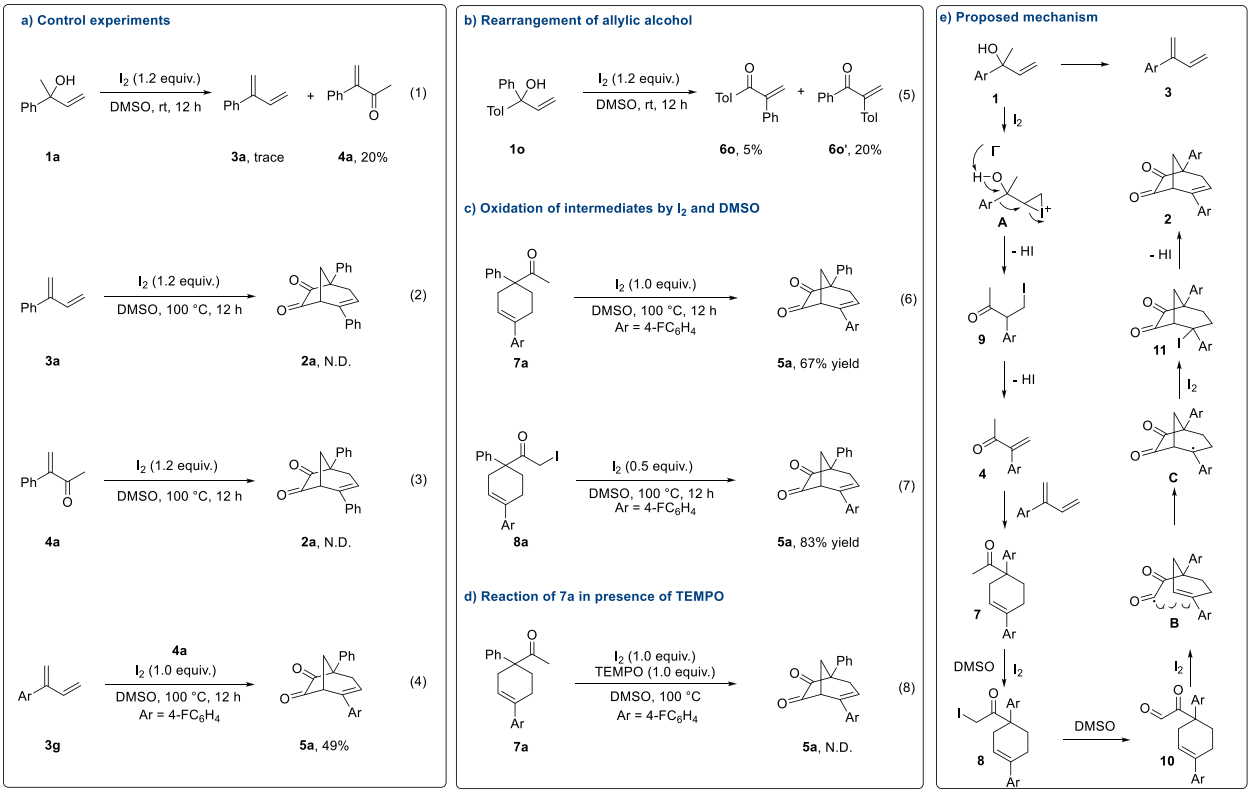

Figure 3. Mechanistic studies and proposed mechanism.

intramolecular radical addition to yield another radical **C**. A further radical quenching of intermediate **C** with iodine produces tertiary iodide **11**. Finally, the elimination of hydrogen iodide from iodide **11** delivers target bicyclo[3.2.1]-octane product **2**.

Guided by the mechanism, we further examined the feasibility of more exciting cross-reaction (Figure 4a). There are many challenges associated with this proposal. (a) The diene intermediate could undergo polymerization and homo-Diels–Alder reaction at high temperatures. (b) In the presence of a Lewis acid, enone is prone to hetero-Diels–Alder reaction. (c) The diene intermediate could be transformed into thiophene in the presence of I_2 and DMSO. (d) Multiple bicyclo[3.2.1]octane products will be generated when two different allylic alcohols are used as starting materials. To our delight, the desired cross-reaction is achieved through careful evaluation of reaction parameters (see Tables S2 and S3 for details). Then, the substrate scope of cross-reaction was explored (Figure 4a). Allylic alcohols bearing electron-withdrawing (**5a**, **5d**, **5f**, and **5g**) and weakly electron-donating substituents (**5b**, **5c**, and **5e**) were all tolerated to give bicyclo[3.2.1]octanes in 43–60% yields. Either substrate **1** or **1′** bearing a methyl group instead of an aryl group could not be transformed into the desired product effectively (**5h** or **5i**, respectively).

Given its privileged ability in the formation of cyclohexenes, Diels–Alder reaction[14] has been integrated into a one-pot construction of highly functionalized bicyclo[3.2.1]octanes (Figure 4b). Different *para* substituents on the phenyl ring of enone furnished the corresponding products **5j**–**5m** in moderate yields, regardless of their electronic properties. The naphthyl-substituted enone reacted smoothly, as well (**5n**). Moreover, alkyl-substituted enone was well tolerated and gave the desired product **5o** in 64% yield. Diene bearing an electron-donating group on the phenyl ring afforded a relatively lower yield (**5p**) compared with those of an electron-withdrawing (**5q**) and neutral diene (**5i**). It is noteworthy that methyl-substituted diene and enone could be adapted to this reaction system, resulting in the target product (**2m**) in 47% isolated yield.

On the contrary, directed functionalization of bicyclo[3.2.1]-octanes could construct elaborate molecular structures that are otherwise difficult to access. As illustrated in Figure 5, reduction of **2a** with $LiAlH_4$ afforded diol **12** in 61% yield. Compound **12** can be used for the synthesis of polysubstituted cyclohexene **13** through C–C bond cleavage followed by reduction.[15] It is interesting to note that only one carbonyl group was reduced to give constitutional isomers **14** and **15** through palladium-catalyzed hydrogenation. Moreover, α-hydroxy ketone **15** could also be transformed into ketone **16** in 47% yield through dehydroxylation.[16] Ring-fused dihydropyrazine **17** was easily prepared in 95% yield by the condensation of diketone **2a** with ethylenediamine.[17] Furthermore, the obtained dihydropyrazine **17** could be further reduced by $NaBH_4$ to enable a rapid assembly of ring-fused piperazine **18** (88% yield).[18] Finally, reaction of alkene **2a** with bromine gave dibromo-bicyclo[3.2.1]octane **19** in 41% yield.[19] The relative configurations of all of the bridged compounds described above were determined by NOESY (nuclear Overhauser effect spectroscopy) spectra. Overall, the transformation described above illustrates well the synthetic potential of this protocol for the bicyclo[3.2.1]octanes and their derivatives.

In conclusion, inspired by a convergent disproportionation, we have developed a strategy for the concise construction of highly functionalized bicyclo[3.2.1]octanes by employing

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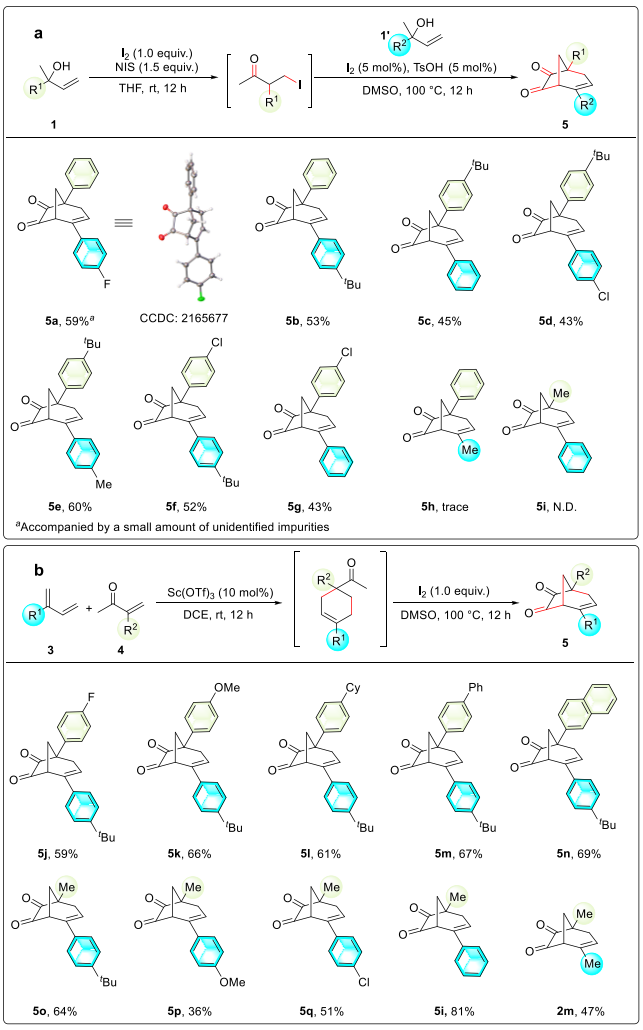

Figure 4. Substrate scope for cross-reaction.

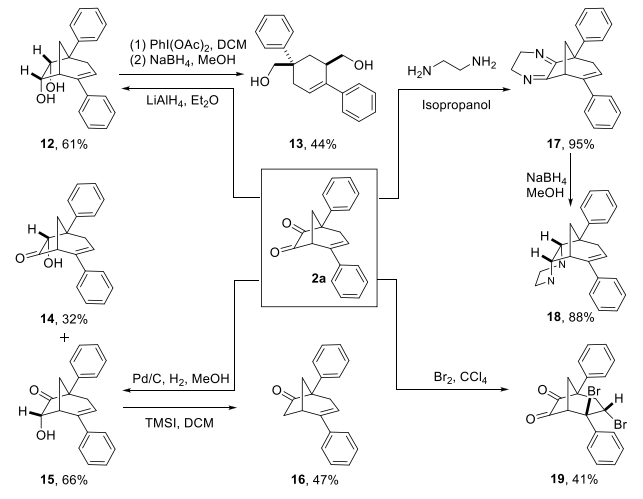

Figure 5. Divergent synthetic transformations of bicyclo[3.2.1]octane.

readily available allylic alcohols as bifunctional blocks. The use of inexpensive iodine and DMSO as oxidants with easy operation makes this protocol practical and sustainable. Guided by mechanistic studies, we established a cross-coupling strategy for the formation of bicyclo[3.2.1]octane from scandium-catalyzed Diels–Alder reaction followed by intramolecular oxidative cyclization. Furthermore, synthetic transformations demonstrated that these products can serve as a versatile platform molecule for the construction of various highly functionalized bicyclo[3.2.1]octanes.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.3c00397.

Optimization details, experimental procedures, analytical and spectroscopic data for new compounds, and copies of NMR spectra (PDF)

Accession Codes

CCDC 2163689 and 2165677 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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